Materials Science Forum Vol 710 (2012) pp 656-661
© (2012) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/MSF.710.656

Online: 2012-01-24

Adhesive Joining of Metal to Metal and Metal to Ceramic by Ceramic Precursor Route

R. Sreeja[1, a], P. V. Prabhakaran[1, b], Sushant. K. Manwatkar[2, c]
and S. Packirisamy[1, d]

[1]Ceramic Matrix Products Division, Propellants & Special Chemicals Group, PCM Entity
Vikram Sarabhai Space Centre, Thiruvananthapuram– 695022, India.
[2] Materials Characterisation Division, Materials & Metallaurgy Group, MME Entity
Vikram Sarabhai Space Centre, Thiruvananthapuram– 695022, India.
[a] r_sreeja@vssc.gov.in, [b]pv_prabhakaran@vssc.gov.in,
[c]sushant_krushnaji@vssc.gov.in, [d]s_packirisamy@ vssc.gov.in

Key words: Geopolymers, ceramic adhesive, alkalisilicates

Abstract

Inorganic ceramic adhesives (geopolymers) based on aluminosilicate matrix are versatile candidates for bonding metals to metals or metals to ceramics. On curing, they result in an amorphous, crosslinked, impervious, acid resistant 3D-structures. Alkali activated aluminosilicate based ceramic adhesive was developed for bonding metals to ceramics and metal to metal, for high temperature applications. The bonding is achieved at 175°C for 3 hrs, by solid state reaction of alkaline solution of allkalisilicate precursor with the refractory filler, contributing to the bulk aluminosilicate matrix. Lap shear strength of 2-4 MPa was obtained for bonding stainless steel. The XRD patterns show the amorphous nature of the aluminosilicate matrix, with mullite formation at higher temperatures. Thermogravimetric analysis shows that the weight loss is only due to the removal of water from the system by means of evaporation and polycondensation of Si-OH groups and Al-OH groups. This is followed by structural reorganisation in which aluminium ions are incorporated into the silicate chains forming the Si-O-Al network resulting in the bonding with the metallic surface. The system can withstand the maximum operational temperatures of the substrates and can be used for bonding different metallic or ceramic, joints/interfaces for RLV-TD/TSTO.

Introduction

Reusable launch vehicles for future space missions require adhesives for joining of different metal alloys and metal-ceramic. Such bonded joints are subjected to different aerothermal conditions for qualifying them for use at different locations. Ceramic adhesives are notable for high temperature capabilities and hence, find application for bonding different metal alloys and also for metal-ceramic bonding, requiring operational temperatures as high as 1000°C. Unlike organic adhesives,

All rights reserved. No part of contents of this paper may be reproduced or transmitted in any form or by any means without the written permission of Trans Tech Publications, www.ttp.net. (ID: 129.93.16.3, University of Nebraska-Lincoln, Lincoln, USA-13/04/15,12:04:09)

ceramic adhesives do not char or degrade at the operational conditions of the joints [1]. Hence, no volatile gases are evolved during the operation which avoids the possibility of adversely affecting the other sensitive components of the system. They are generally based on alkali silicates and various metal phosphates mixed with powder fillers such as carbon, alumina, silica, magnesia and zirconia [1]. During the curing process, the binding agent may melt and/or undergoes reaction with the added fillers to form a refractory ceramic bond. Ceramic adhesives retain bond integrity to much higher temperatures of 1300-1400°C but once cured are brittle and unable to relieve stresses generated during thermal cycling. This can be avoided to a great extent by the proper incorporation of fillers with similar coefficient of thermal expansion (CTE), so as to avoid large CTE mismatch with the bonding substrates with increase in temperature [1,2].

Alkali activated aluminosilicate based ceramic materials also known as geopolymers possess excellent physico-chemical and mechanical properties, which include low density, microporosity or nano-porosity, negligible shrinkage, high strength, thermal stability, high surface hardness, fire and chemical resistance. They have high melting points but can undergo structural transformations at lower temperatures without causing the materials to change dimension and porosity [3]. These desirable properties render these materials as ceramic adhesives. These adhesives are similar to water glass and silica sol-based adhesives, but have much lower water to ceramic ratios [1]. Compared to typical refractory adhesives available, geopolymers do not require multiple high temperature curing steps. On curing, they result in an amorphous, crosslinked, impervious, acid resistant 3D-structures of Si-O-Al and Si-O-Si bonds arranged in a solid amorphous aluminosilcate network [1]. The Al^{3+} is in IV fold co-ordination and is charge balanced by an alkali cation such as K^+ or Na^+. The alkali silicate solid or liquid solution is used for dissolution of raw materials to form reactive precursors required for geopolymerization [3].

The present study involves the development of alkali activated aluminosilicate matrix materials such as mica and kaolin mixed with reactive ceramic precursors which forms aluminosilicate matrix by sol-gel transformations and finally get hardened into solid aluminosilicate at high temperatures. The adhesive has been used for bonding metal alloys like stainless steel and also for bonding silica tile and inconel. The ceramic material has been characterized by XRD, TGA and compressive strength to understand the structural transformations taking place during heat treatment at different temperatures. The adhesive lap shear strength of the ceramic adhesive has been evaluated.

Experimental

Materials and Methods: The mixture containing solid potassium silicate (Surabhi Industries, Pune) and refractory fillers viz alumina (Alfa Aesar), mica (Surabhi Industries, Pune), and kaolin (Surabhi Industries, Pune) was ball milled for 8 h and the effective Si/Al mole ratio was 2.3. The mixture was then made into a paste with 2M KOH solution. The water to solid mass ratio was 0.24. The paste was used for bonding stainless steel LSS coupons, cleaned using detergent and water, and cured at 175°C for 3 hrs and single lap shear strength was evaluated as per ASTM D1002. The paste was also cured separately and the cured powder was made into pellets of size 3 mm dia and 10 mm height and heat treated to different temperatures under air to get samples for evaluation of compressive strength. The heat treated powder samples was also characterised by XRD (Philips 1729 instrument using Cu-Kα radiation. TG studies were carried out using TA instrument SDT Q600.

Results and Discussion

Figure 1 shows the XRD patterns obtained for samples heat treated to different temperatures. The XRD patterns show the characteristic amorphous nature of geopolymers with some crystalline peaks of Al_2O_3, silica and silicates. The broad humps registered between 2θ = 20° and 2θ = 35° can be attributed to the presence of amorphous silicate chains consisting of SiO_4 and SiO_2 chain structure with crystalline peaks of microcline ($KAlSi_3O_8$) and unreacted Al_2O_3 [4]. The peak corresponding to SiO_4 and Al_2O_3 units is reduced at higher temperatures which show the dissolution of SiO_4 units to form Si-O-Al linkages and hence the amorphous character gradually increases. The maximum intense peak at 27.17° confirms the geopolymer reaction between the alkali silicate and solid aluminosilicate oxides [5, 6]. The formation of mullite is also confirmed at higher temperatures of 900°C.

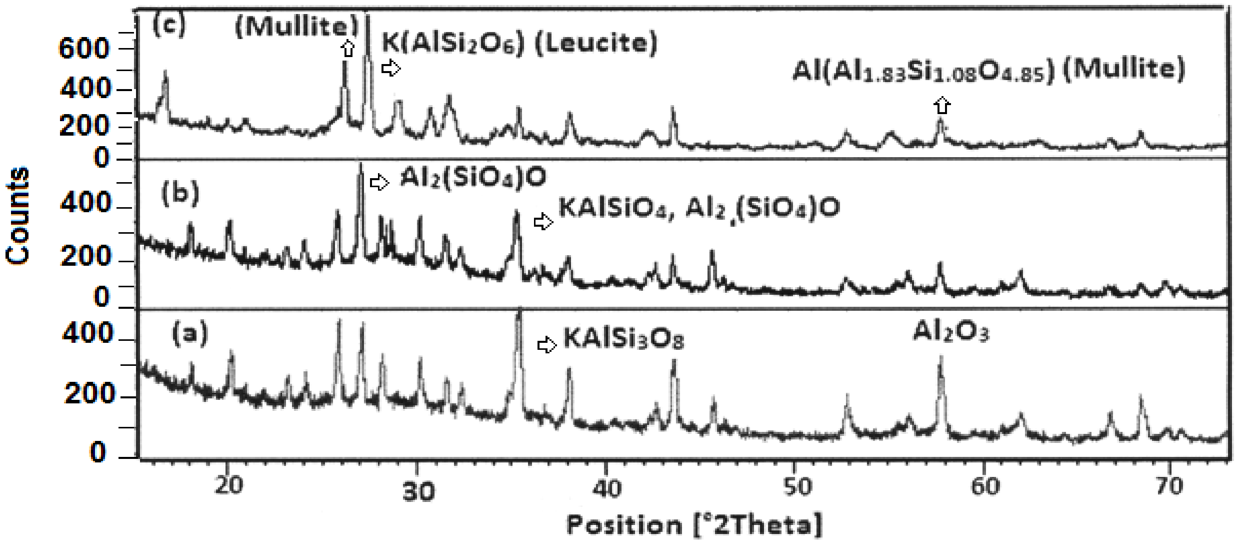

Figure 1: XRD of samples heat treated to different temperatures: (a) 300°C (b) 500°C and (c) 900°C

Figure 2 shows the TG/DSC curve of the cured sample from RT to 900°C with a heating rate of 10°C/min in air atmosphere. The total weight loss is 21% at 1200°C, of which 10 % wt loss occurs below 200°C which is attributed to the loss of free water and moisture absorbed by the sample due to the presence of unreacted potassium silicate in the adhesive. The endothermic peak is due to the loss of free water and water formed due to the condensation polymerisation of ≡SiOH groups and $Al(OH)_3$ to form aluminosilicate gel. The exothermic peak at 400°C is due to the phase change of kaolin to amorphous metakaolin[5]. The remaining weight loss can be attributed to the removal of residual water from the gel and thus undergoes a solid state transformation to form the final hardened adhesive at 500°C. At 1000°C an endothermic reaction is observed and it can be attributed to the final reaction between SiO_2 released from metakaolin at this temperature and alumina to form hard aluminosilicate matrix [5]. After 500°C, practically no weight loss is observed and hence can be used for high temperature applications.

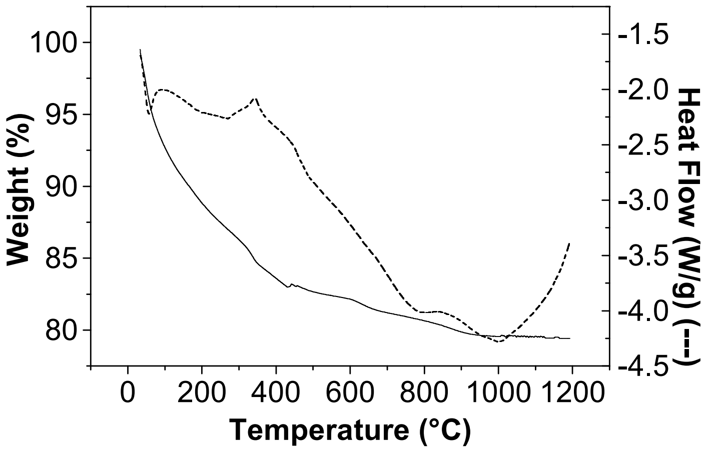

Figure 2: TG/DSC curves for cured sample

Figure 3 shows compressive strength of samples heat treated to different temperatures from 175°C to 1300°C. The compressive strength of the aluminosilicate matrix increased from 0.24 MPa to 63 MPa at 1100°C. A sudden increase in compressive strength after 500°C confirms the completion of polymerization reaction resulting in the formation of hard solid aluminosilicate matrix. An increase in compressive strength for samples heat treated to above 900°C is due to the further hardening of the matrix by the reaction between alumina and silica released from metakaolin in the matrix to form mullite [3].

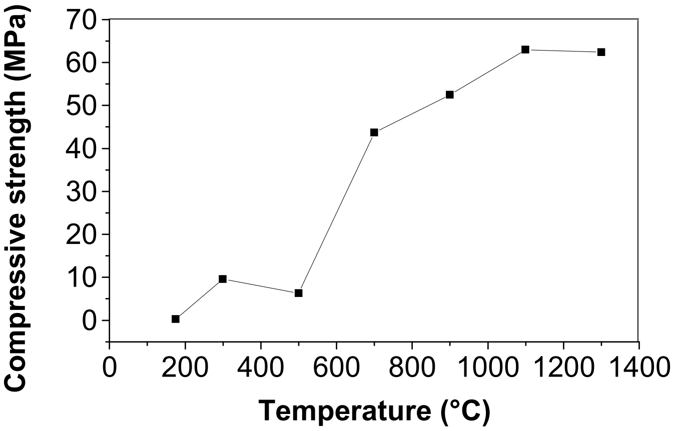

Figure 3: Compressive strength of samples vs heat treatment temperature

Lap shear strength of 2-4 MPa at RT was obtained for stainless steel LSS coupons heat treated to different temperatures from 175°C to 500°C. Figure 4 shows the fractured surface of single lap shear joint specimens. The failure was cohesive in the adhesive which shows correct surface preparation. The adhesive was also used for inconel-silica tile bonding. The bonding remains intact even after heating to 500°C in a muffle furnace (Figure5). The reaction involves an -OH promoted hydrolysis reaction, followed by condensation reaction of the hydroxylated species (≡SiOH and $Al(OH)_3$) to form aluminosilciate gel as an inorganic polymeric matrix. The reactive hydroxylated (≡SiOH) species is coming from the dissolution of solid potassium silicate by reaction with alkali and water and results in the gradual release of silica to the geopolymer gel. The presence of kaolin in the reaction mixture also results in the release of silica into the geopolymer gel for further reaction with alumina at high temperatures of 1000°C and results in the formation of mullite. The final matrix is a mixture of mullite and silica. Water is the only by product because of polycondensation reaction and the reaction is completed at around 500°C, after which it remain intact up to around 1300°C.

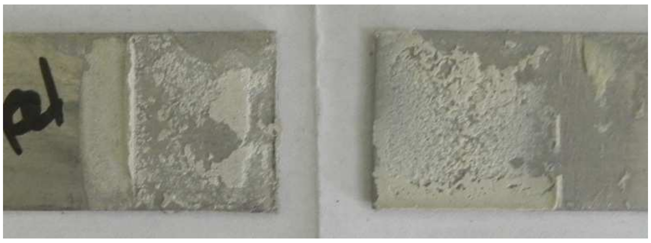

Figure 4: Fractured surface of single lap joint specimen

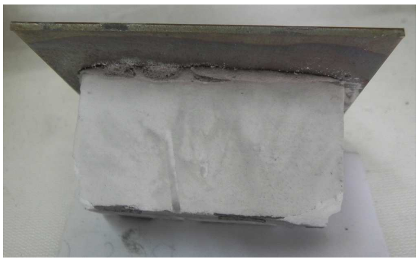

Figure 5: Inconel/silica tile bonded specimen after heated to 500°C in a muffle furnace

Conclusions

The aluminosilicate based ceramic adhesive developed by ceramic precursor route can be used for bonding stainless steel for applications of shear strength of 2-4 MPa. It can also be used for inconel-ceramic bonding. The geopolymerization reaction occurs at lower temperatures of 100-200°C and hence, the joints heat treated to ~175-200°C can be used as such without heat treating them at high temperatures. During the actual operational conditions of high temperatures further reactions leading to the formation of mullite takes place resulting in very hard joints. The bonding technique is highly cost effective as it does not involve sophisticated instruments and the raw materials used for adhesive are also very cheap and easily available. The adhesive can also be used for bonding other metal alloys which do not get affected due to high alkalinity of the geopolymer.

Acknowledgement

The authors would like to thank the Analytical and Spectroscopy Division (ASD) for thermal and mechanical analyses and materials Characterisation division (MCD) for XRD analysis.

References:

[1] J. Davidovits, Geopolymer Polymeric Inorganic New Materials, J. Therm. Anal. 37 (1991) 1633-1656.

[2] J. B. Schutz and T. F. Barton, U. S. Patent 6.402,156. (2002)

[3] D. Fullston and K. Sagoe-Crentsil, Small Footprint Aluminosilicate Matrix-Refactory Hybrid Materials, J. Aust. Ceram. Soc. 45 (2) (2009) 69-74.

[4] D. Dimas, I. Glannopoulou, D. Panias, Polymerisation in Sodium Silicate Solutions: A Fundamental Process in Geopolymerisation Technology, J. Mater. Sci. 44 (2009) 3719-3730.

[5] M. C. Mayoral, M. T. Izquierdo, J. M. Andres, B. Rubio, Aluminosilicates Transformations in Combustion Followed by DSC, Thermochim. Acta. 373 (2001) 173-180.

[6] F. M. Wahl, R. E. Grim, R. B. Graf, Phase Transformations in Silica-Alumina Mixtures as Examined by Continuous X-Ray Diffractions, The Am. Min. 46 (1961) 1064-1076.

Advances in Metallic Materials and Manufacturing Processes for Strategic Sectors
10.4028/www.scientific.net/MSF.710

Adhesive Joining of Metal to Metal and Metal to Ceramic by Ceramic Precursor Route
10.4028/www.scientific.net/MSF.710.656